Biophysical Chemistry, 39 (1991) 191–198
© 1991 Elsevier Science Publishers B.V. (Biomedical Division) 0301-4622/91/$03.50

BIOCHE 01539

On the electrophoretic mobility of biological cells

Hiroyuki Ohshima and Tamotsu Kondo

Faculty of Pharmaceutical Sciences and Institute of Colloid and Interface Science, Science University of Tokyo, Shinjuku-ku, Tokyo 162, Japan

Received 22 May 1990
Revised manuscript received 3 September 1990
Accepted 10 September 1990

Electrophoretic mobility; Biological cell

A theoretical study has been performed on the electrophoretic mobility of a large colloidal particle with a surface charge layer as a model for biological cells. An approximate mobility expression is derived which is applicable to the general case of an arbitrary distribution of membrane-fixed charges. This expression consists of two terms: the first is a weighted average of potentials over the surface charge layer, while the second is that of the volume density of membrane-fixed charges and does not depend on the electrolyte concentration. At high electrolyte concentrations (corresponding to physiological conditions), where the potentials are very low owing to the shielding effects of electrolytes, the first term diminishes so that the mobility is determined mainly by the second term. This means that a particle with zero surface potential can exhibit a non-zero mobility, in contrast to the prediction from the classical Smoluchowski theory. Comparison is also made with the theory of Hermans and Fujita for the electrophoresis of polyelectrolytes.

1. Introduction

The measurement of the electrophoretic mobility of biological cells provides us with information on the electric properties of the cell surface. Usually the mobility is converted to the zeta potential of cells via the Smoluchowski equation. This equation, however, holds for ion-impenetrable solid surfaces and thus should not be applied to biological cells, whose surfaces are normally covered by ion-penetrable layers composed of charged polymers. Several theoretical studies [1–7] have been carried out on the electrophoresis of colloidal particles with structured surfaces as a model for cells. Ohshima and Kondo [7], in particular, have derived an approximate mobility expression for particles with surface layers in which fixed charges are uniformly distributed. This expression consists of two terms: the first is a weighted average of the surface potential and the Donnan potential, and the second is directly related to the membrane-fixed charges and is not subject to shielding effects of electrolyte ions. In the present paper, we shall demonstrate that a similar result generally holds for colloidal particles with an arbitrary distribution of membrane-fixed charges and that under physiological conditions the mobility is determined mainly by the term independent of the ionic shielding effects. This behavior at high electrolyte concentrations is also predicted in the theories of the electrophoresis of polyelectrolytes [8–10]. We shall compare our theory particularly with the theory of Hermans and Fujita [9].

2. Basic equations

Consider a colloidal particle moving with velocity U in a liquid containing a symmetrical electrolyte of valency υ and bulk concentration n in an

Correspondence address: T. Kondo, Faculty of Pharmaceutical Sciences, Science University of Tokyo, 12, Ichigaya Funagawara-machi, Shinjuku-ku, Tokyo 162, Japan.

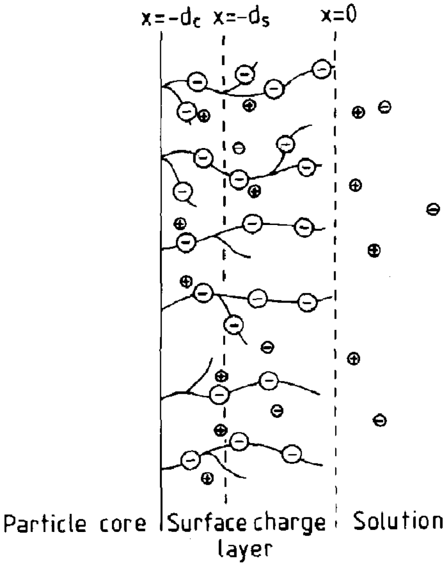

Fig. 1. Schematic representation of the ion-penetrable surface layer of thickness d_c composed of negatively charged polymers (represented by large circles with minus sign). Mobile electrolyte ions are represented by small circles with + or − signs. The slipping plane is located at $x = -d_s$ $(0 \leqq d_s \leqq d_c)$.

applied field E. The particle is covered with a surface charge layer of thickness d_c composed of charged polymers. The particle radius is much larger than $1/\kappa$ (κ, Debye-Hückel parameter) so that the particle surface can be assumed to be planar and the applied field E to be parallel to the surface. We take an x-axis to be perpendicular to the surface with its origin at the boundary between the surface charge layer and the surrounding solution (fig. 1). In the surface charge layer, membrane fixed charges are distributed at a density of $\rho_{\text{fix}}(x)$. We assume that the slipping plane, at which the liquid velocity relative to the particle is zero, is located at $x = -d_s$ inside the surface charge layer $(0 \leqq d_s \leqq d_c)$.

The electric potential $\psi(x)$ at position x relative to the bulk solution phase, where $\psi(x)$ is set equal to zero, is related to the space charge density $\rho(x)$ at the same point by the Poisson equation:

$$\frac{d^2\psi}{dx^2} = -\frac{\rho(x)}{\epsilon_r\epsilon_0} \tag{1}$$

where ϵ_r is the relative permittivity of the solution and ϵ_0 the permittivity of a vacuum. We assume a Boltzmann distribution for electrolyte ions. Then, the concentrations of cations, $n_+(x)$, and anions, $n_-(x)$, are given by

$$n_\pm(x) = n \exp(\mp ve\psi/kT), \tag{2}$$

where e is the elementary electric charge, k Boltzmann's constant and T the absolute temperature. The space charge density resulting from electrolyte ions, $\rho_{\text{el}}(x)$, is expressed as

$$\begin{aligned}\rho_{\text{el}}(x) &= ve\left[n_+(x) - n_-(x)\right]\\ &= -2nve \sinh(ve\psi(x)/kT).\end{aligned} \tag{3}$$

For the region $x > 0$, $\rho(x)$ is given only by $\rho_{\text{el}}(x)$,

$$\rho(x) = \rho_{\text{el}}(x), \quad x > 0, \tag{4}$$

while for $-d_c < x < 0$, $\rho(x)$ is given by the sum of $\rho_{\text{el}}(x)$ and $\rho_{\text{fix}}(x)$, viz.,

$$\rho(x) = \rho_{\text{el}}(x) + \rho_{\text{fix}}(x), \quad -d_c < x < 0. \tag{5}$$

Combining eqs 1 and 3–5, we obtain the following Poisson-Boltzmann equations for $\psi(x)$:

$$\frac{d^2\psi}{dx^2} = -\frac{\rho_{\text{el}}(x)}{\epsilon_r\epsilon_0} \tag{6}$$

$$= \frac{2nve}{\epsilon_r\epsilon_0}\sinh\frac{ve\psi}{kT}, \quad x > 0, \tag{6a}$$

$$\frac{d^2\psi}{dx^2} = -\frac{\rho_{\text{el}}(x) + \rho_{\text{fix}}(x)}{\epsilon_r\epsilon_0} \tag{7}$$

$$= \frac{2nve}{\epsilon_r\epsilon_0}\sinh\frac{ve\psi}{kT} - \frac{\rho_{\text{fix}}(x)}{\epsilon_r\epsilon_0}, \quad -d_c < x < 0. \tag{7a}$$

The boundary conditions are

$$\psi(-0) = \psi(+0), \tag{8}$$

$$\left.\frac{d\psi}{dx}\right|_{x=-0} = \left.\frac{d\psi}{dx}\right|_{x=+0}, \tag{9}$$

$$\left.\frac{d\psi}{dx}\right|_{x=-d_c} = 0. \tag{10}$$

Eqs 8 and 9 are the continuity conditions of ψ and of $d\psi/dx$ at $x = 0$. In eq. 10 the contribution from the electric field within the particle core has been ignored.

The flow velocity of the surrounding liquid (relative to the particle), which we denote by $u(x)$, is parallel to the particle surface. The Navier-Stokes equations for $u(x)$ are then

$$\eta \frac{\mathrm{d}^2 u}{\mathrm{d}x^2} + \rho_{\mathrm{el}}(x) E = 0, \quad x > 0, \tag{11}$$

$$\eta \frac{\mathrm{d}^2 u}{\mathrm{d}x^2} - \gamma u + \rho_{\mathrm{el}}(x) E = 0, \quad -d_{\mathrm{s}} < x < 0, \tag{12}$$

where η is the viscosity and γ the frictional coefficient of the surface charge layer. The term $-\gamma\ u$ arises from the drag force exerted by the polymer segments in the surface charge layer upon the liquid. Terms due to a pressure gradient do not appear in eqs 11 and 12, since the particle surface is assumed to be an infinitely large planar surface so that the pressure has the same value in the direction parallel to the particle surface. The boundary conditions for $u(x)$ are

$$u(-d_{\mathrm{s}}) = 0, \tag{13}$$

$$u(-0) = u(+0), \tag{14}$$

$$\left.\frac{\mathrm{d}u}{\mathrm{d}x}\right|_{x=-0} = \left.\frac{\mathrm{d}u}{\mathrm{d}x}\right|_{x=+0}, \tag{15}$$

$$u \xrightarrow[x \to +\infty]{} -U. \tag{16}$$

Eq. 13 expresses the situation where the slipping plane is located at $x = -d_{\mathrm{s}}$. Eqs 14 and 15 are the continuity conditions of $u(x)$ and of $\mathrm{d}u/\mathrm{d}x$ at $x = 0$. Eq. 16 states that the liquid velocity in the bulk solution phase relative to the particle is equal to the electrophoretic velocity with its sign altered. By replacing $\rho_{\mathrm{el}}(x)$ with $-\epsilon_{\mathrm{r}}\epsilon_0 \mathrm{d}^2\psi/\mathrm{d}x^2$ in eq. 11 and with $-\epsilon_{\mathrm{r}}\epsilon_0 \mathrm{d}^2\psi/\mathrm{d}x^2 - \rho_{\mathrm{fix}}(x)$ in eq. 12, with the help of eqs 6 and 7, one can integrate eqs 11 and 12 to obtain

$$u(x) = \frac{\epsilon_{\mathrm{r}}\epsilon_0 E}{\eta} \psi(x) - U, \quad x > 0, \tag{17}$$

$$\begin{aligned} u(x) = {} & \frac{\epsilon_{\mathrm{r}}\epsilon_0 E}{\eta} \Bigg[\psi(x) - \frac{\psi(-d_{\mathrm{s}})}{\cosh \lambda d_{\mathrm{s}}} \cosh \lambda x \\ & - \left\{ \frac{\lambda}{\cosh \lambda d_{\mathrm{s}}} \int_{-d_{\mathrm{s}}}^{0} \psi(x) \cosh \lambda x \, \mathrm{d}x \right\} \\ & \times \sinh \lambda (x + d_{\mathrm{s}}) \\ & + \lambda \int_{-d_{\mathrm{s}}}^{x} \psi(x') \sinh \lambda (x - x') \, \mathrm{d}x' \Bigg] \\ & + \frac{E}{\eta\lambda} \Bigg[\int_{-d_{\mathrm{s}}}^{x} \rho_{\mathrm{fix}}(x') \sinh \lambda (x - x') \, \mathrm{d}x' \\ & - \left(\int_{-d_{\mathrm{s}}}^{0} \rho_{\mathrm{fix}}(x) \cosh \lambda x \, \mathrm{d}x \right) \\ & \times \frac{\sinh \lambda (x + d_{\mathrm{s}})}{\cosh \lambda\ d_{\mathrm{s}}} \Bigg], \\ & -d_{\mathrm{s}} < x < 0, \end{aligned} \tag{18}$$

where

$$\lambda = (\gamma/\eta)^{1/2}. \tag{19}$$

Using eq. 17, the electrophoretic mobility μ can be expressed as

$$\begin{aligned} \mu &= \frac{U}{E} \\ &= -\frac{u(0)}{E} + \frac{\epsilon_{\mathrm{r}}\epsilon_0}{\eta} \psi(0), \end{aligned} \tag{20}$$

Evaluating $u(0)$ via eq. 18 and substituting the result into eq. 20, we obtain the following general formula for the electrophoretic mobility:

$$\begin{aligned} \mu = {} & \frac{\epsilon_{\mathrm{r}}\epsilon_0}{\eta} \frac{1}{\cosh \lambda d_{\mathrm{s}}} \\ & \times \left[\psi(-d_{\mathrm{s}}) + \lambda \int_{-d_{\mathrm{s}}}^{0} \psi(x) \sinh \lambda (x + d_{\mathrm{s}}) \, \mathrm{d}x \right] \\ & + \frac{1}{\eta\lambda} \frac{1}{\cosh \lambda\ d_{\mathrm{s}}} \\ & \times \int_{-d_{\mathrm{s}}}^{0} \rho_{\mathrm{fix}}(x) \sinh \lambda (x + d_{\mathrm{s}}) \, \mathrm{d}x. \end{aligned} \tag{21}$$

3. Results and discussion

We have derived a general mobility formula, eq. 21, for a large colloidal particle with a surface charge layer as a model for biological cells. For typical cells such as human erythrocytes, d_{s} amounts to 50–100 Å and $1/\lambda$ is estimated to be of the order of 10 Å [7]. For such cases, i.e., when the condition $\lambda d_s \gtrsim 1$ is fulfilled, eq. 21 reduces to

$$\mu = \frac{\epsilon_r\epsilon_0}{\eta}\left[\overline{\psi(x)} + \frac{1}{\lambda^2}\frac{\overline{\rho_{\text{fix}}(x)}}{\epsilon_r\epsilon_0}\right], \tag{22}$$

where

$$\overline{f(x)} = \lambda\int_{-\infty}^{0} f(x)e^{\lambda x}\,\mathrm{d}x \tag{23}$$

is a weighted average of $f(x)$ over the surface charge layer (the lower limit of the integration, $-d_s$, has been replaced by $-\infty$ with negligible error). Further simplification can be made for the special case of uniform fixed-charge distribution within the surface charge layer, by employing an approximate form of the solution to the Poisson-Boltzmann equation (eq. 7a). We assume that charged groups of valency z are distributed at a uniform density N, viz.,

$$\rho_{\text{fix}} = zeN. \tag{24}$$

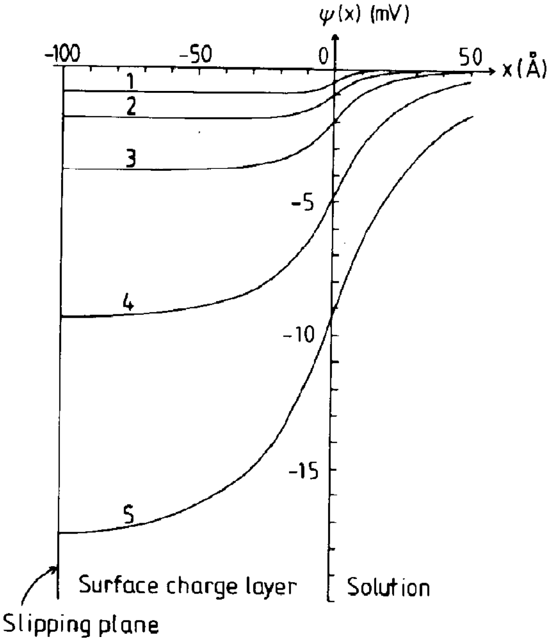

Fig. 2. The potential distribution $\psi(x)$ across the uniformly charged surface layer for several values of n, calculated with $\upsilon = 1$, $z = -1$, $N = 0.015$ M, $d_c = d_s = 100$ Å, $\epsilon_r = 78.5$ and $T = 298$ K. Curves: (1) $n = 0.2$ M; (2) $n = 0.1$ M; (3) $n = 0.05$ M; (4) $n = 0.02$ M; (5) $n = 0.01$ M. The density N of charged groups is given in units of M so that N and n have the same unit.

In this case, if $d_c \gtrsim 1/\kappa$ (κ is defined later in eq. 29), then the potential far inside the surface charge layer is in practice equal to the Donnan potential and the potential varies nearly exponentially not only outside but also inside the surface charge layer, as demonstrated in the examples given in fig. 2 (which are calculated via eqs 6a and 7a). The potential distribution inside the surface charge layer is thus approximated by [5–7]

$$\psi(x) = \psi_{\text{DON}} + [\psi_0 - \psi_{\text{DON}}]\exp(\kappa_m x), \quad -d_c < x < 0, \tag{25}$$

with

$$\psi_{\text{DON}} = \frac{kT}{\upsilon e}\operatorname{arcsinh}\left(\frac{zN}{2\upsilon n}\right) = \frac{kT}{\upsilon e}\ln\left[\frac{zN}{2\upsilon n} + \left\{\left(\frac{zN}{2\upsilon n}\right)^2 + 1\right\}^{1/2}\right], \tag{26}$$

$$\psi_0 = \psi_{\text{DON}} - \frac{\upsilon e}{kT}\tanh\left(\frac{\upsilon e\psi_{\text{DON}}}{2kT}\right) = \frac{kT}{\upsilon e}\left(\ln\left[\frac{zN}{2\upsilon n} + \left\{\left(\frac{zN}{2\upsilon n}\right)^2 + 1\right\}^{1/2}\right] + \frac{2\upsilon n}{zN}\left[1 - \left\{\left(\frac{zN}{2\upsilon n}\right)^2 + 1\right\}^{1/2}\right]\right), \tag{27}$$

$$\kappa_m = \kappa\cosh^{1/2}(\upsilon e\psi_{\text{DON}}/kT) = \kappa\left[1 + (zN/2\upsilon n)^2\right]^{1/4}, \tag{28}$$

$$\kappa = \left(2n\upsilon^2e^2/\epsilon_r\epsilon_0 kT\right)^{1/2}, \tag{29}$$

where ψ_{DON} represents the Donnan potential of the surface charge layer, $\psi_0 = \psi(0)$ is the potential at $x = 0$, which we call the surface potential, κ denotes the Debye-Hückel parameter and κ_m is the effective Debye-Hückel parameter of the surface charge layer. For biological cells, $d_c \approx 50$–100 Å and $1/\kappa$ (i.e., the thickness of the double layer formed outside and inside the surface charge layer) amounts to 10 Å under physiological conditions so that the condition $d_c \gtrsim 1/\kappa$ is satisfied.

Note that the potential distribution (eq. 25) does not depend on d_s or d_c. Substituting this result into eq. 22 yields

$$\mu = \frac{\epsilon_r\epsilon_0}{\eta}\frac{\psi_0/\kappa_m + \psi_{DON}/\lambda}{1/\kappa_m + 1/\lambda} + \frac{zeN}{\eta\lambda^2}, \tag{30}$$

a result previously obtained [7]. In the limit of very large frictional constant γ (or, $1/\lambda \to 0$), the slipping plane coincides with $x = 0$ so that ψ_0 becomes equal to the zeta potential and eq. 30 reduces to the well-known Smoluchowski mobility formula for a solid colloidal particle [11],

$$\mu = \frac{\epsilon_r\epsilon_0}{\eta}\psi_0. \tag{31}$$

The mobility formulas (eqs 22 and 30) consist of two terms: the first is a weighted average of potentials $\psi(x)$ over the surface charge layer and the second is that of the membrane-fixed charges $\rho_{fix}(x)$. In eq. 30, in particular, the first term is a weighted average of the Donnan potential and the surface potential. It should be stressed that only the first term is subject to the shielding effects of electrolytes, tending to zero as the electrolyte concentration increases, while the second term does not depend on the electrolyte concentration n. In the limit of high electrolyte concentration, all the potentials vanish and only the second term of the mobility expression remains, viz.,

$$\begin{aligned}\mu &\xrightarrow[n \to \infty]{} \mu_\infty \\ &= \frac{\overline{\rho_{fix}(x)}}{\eta\lambda^2} \\ &= \frac{\overline{\rho_{fix}(x)}}{\gamma}.\end{aligned} \tag{32}$$

Note that the Smoluchowski formula (eq. 31) does not have this term and tends to zero in the limit of high electrolyte concentration. Also, it should be borne in mind that the mobility formulas, eqs 22 and 30, do not depend on the value of d_s. This means that the mobility of particles with structured surfaces is insensitive to the precise position of the slipping plane. In other words, for such cases, the zeta potential loses its meaning.

Consider the case of uniform fixed-charge distribution, i.e., $\rho_{fix}(x) = zeN$ in more detail. In this case, we have

$$\mu_\infty = \frac{zeN}{\eta\lambda^2} = \frac{zeN}{\gamma}. \tag{33}$$

This term can be interpreted as resulting from the balance between the electric force acting on the membrane fixed charges ($zeNE$) and the frictional forces (γu), viz.,

$$\gamma u + zeNE = 0. \tag{34}$$

Indeed, in the middle region of the surface charge layer where $d^2u/dx^2 = 0$, at complete shielding of electrolytes the Navie-Stokes equation (eq. 12) reduces to eq. 34, since $d^2\psi/dx^2 = 0$ and $\rho_{el}(x) + zeN = 0$ (which is the electroneutrality condition). In order to establish the magnitude of the contribution of μ_∞, we consider the velocity distribution $u(x)$ of liquid flow across the surface charge layer. For the case where the fixed-charge distribution is uniform and $\lambda\ d_c \geq \lambda\ d_s \gtrsim 1$, the velocity distribution $u(x)$ (eq. 18) can be approximated by

$$\begin{aligned}u(x) = {}& \frac{\epsilon_r\epsilon_0 E}{\eta}(\psi_0 - \psi_{DON}) \\ &\times \frac{\kappa_m[\kappa_m \exp(\kappa_m x) - \lambda \exp(\lambda x)]}{\kappa_m^2 - \lambda^2} \\ &+ \frac{zeNE}{\eta\lambda^2}[\exp(-\lambda(x + d_s)) - 1], \\ &- d_s < x < 0.\end{aligned} \tag{35}$$

Examples of $u(x)$ calculated via eq. 35 (for $-d_s < x < 0$) and eq. 17 (for $x > 0$) at several values of the electrolyte concentration n are plotted in fig. 3 (curves with the same number in figs 2 and 3 correspond to the same condition), showing large contribution from μ_∞. In the middle region of the surface charge layer, all the terms that decay as $\exp(\kappa_m x)$, $\exp(\lambda x)$ or $\exp(-\lambda(x + d_s))$ with decay constants $1/\kappa_m$ or $1/\lambda$ vanish so that

$$u(x) \approx -\frac{zeNE}{\eta\lambda^2} = -\mu_\infty E. \tag{36}$$

It is this term that yields the term independent of the electrolyte concentration. We also see from eq.

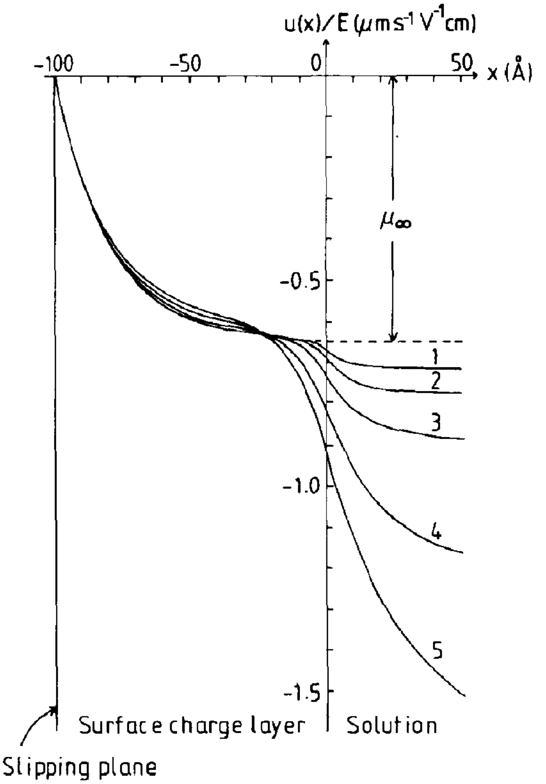

Fig. 3. The velocity distribution of liquid flow $u(x)$ across the uniformly charged surface layer for several values of n, calculated with $v=1$, $z=-1$, $N=0.015$ M, $d_c=d_s=100$ Å, $1/\lambda = 20$ Å, $\eta = 0.891\times10^{-3}$ N m^{-2} s, $\epsilon_r = 78.5$ and $T=298$ K. Curves: (1) $n=0.2$ M; (2) $n=0.1$ M; (3) $n=0.05$ M; (4) $n=0.02$ M; (5) $n=0.01$ M. The value of $-u(+\infty)/E$ gives the mobility μ. The dashed line indicates the contribution from the term independent of the electrolyte concentration, μ_∞.

35 that $1/\lambda$ can be interpreted as the distance between the slipping plane and the bulk membrane phase where $u(x)$ is given by eq. 36.

It can be shown from eqs 26–28 that at low N, ψ_0 and ψ_{DON} both become proportional to N, viz.,

$$\psi_{\mathrm{DON}} = 2\psi_0 = \frac{kT}{ve}\,\frac{zN}{2vn}, \qquad (37)$$

and

$$\kappa_m \approx \kappa, \qquad (38)$$

so that eq. 30 becomes

$$\mu = \frac{zeN}{\eta\lambda^2}\left[1+\left(\frac{\lambda}{\kappa}\right)^2\frac{1+\lambda/2\kappa}{1+\lambda/\kappa}\right]. \qquad (39)$$

This approximation will be valid for biological cells, because as will be seen later, if the mobility of cells is analyzed with the present theory, the predicted surface potential of cells turns out to be considerably lower than that expected via Smoluchowski's theory. In this case, the ratio of the contribution of μ_∞ to the total mobility μ becomes a simple function of only λ/κ, viz.,

$$\frac{\mu_\infty}{\mu} = \frac{1+(\lambda/\kappa)}{1+(\lambda/\kappa)+(\lambda/\kappa)^2+(\lambda/\kappa)^3/2}. \qquad (40)$$

The ratio μ_∞/μ is plotted in fig. 4 as a function of the electrolyte concentration n for several values of $1/\lambda$. We observe that at high electrolyte concentrations, corresponding to usual physiological conditions, this ratio is very high. That is, the mobility is determined mainly by μ_∞. This term arises from the liquid flow inside the surface charge

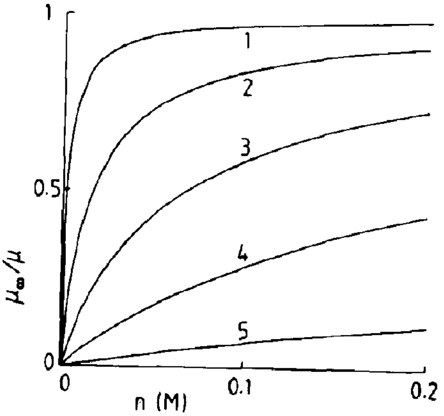

Fig. 4. The ratio of μ_∞ to the total mobility μ as a function of n for several values of $1/\lambda$ at low N, calculated with $v=1$, $\epsilon_r = 78.5$ and $T=298$ K. Curves: (1) $1/\lambda = 50$ Å; (2) $1/\lambda = 20$ Å; (3) $1/\lambda = 10$ Å; (4) $1/\lambda = 5$ Å; (5) $1/\lambda = 2$ Å.

layer, i.e., an electrophoresis mechanism that is not considered in Smoluchowski's theory. In Smoluchowski's theory it is the surface potential (to be exact, the zeta potential, i.e., the potential at the slipping plane) that results in the electrophoretic motion of colloidal particles. This means that in Smoluchowski's theory, particles with zero surface potentials cannot move in an external electric field. Our theory, on the other hand, predicts non-zero mobilities even if the surface potential is zero (of course, $\rho_{\mathrm{fix}}(x) \neq 0$ (or $N \neq 0$) is required for non-zero mobilities).

The existence of a non-vanishing part in the mobility at high electrolyte concentrations is the most remarkable difference between Smoluchowski's theory and our results. Measurements of the electrophoretic mobility of human erythrocytes [12] show that the mobility tends to a non-zero value at high electrolyte concentration. This value should correspond to μ_∞ in our theory. The observation of non-zero mobilities cannot be explained by the classical Smoluchowski theory. This implies that the motion of human erythrocytes in an electric field follows the electrophoresis mechanism that we have proposed. For example, in our theory at $n = 0.1$ M, $N = 0.01$ M, $1/\lambda = 20$ Å, $\epsilon_r = 78.5$ and $T = 298$ K, in spite of the fact that the surface potential ψ_0 is -1 mV (curve 2 in fig. 3), the mobility μ amounts to -0.78 μm s^{-1} V^{-1} cm. With Smoluchowski's formula, on the other hand, this mobility value is converted to the surface potential (or zeta potential) of approx. -10 mV. That is, Smoluchowski's formula would yield a considerable overestimate of the surface potential. We would like to suggest that in order to analyze the mobility data of cells with structured surfaces, the mobility formula, eq. 21, or its approximate forms (eqs 22, 30, and 39) should be employed, instead of Smoluchowski's formula. An analysis of the mobility data of human erythrocytes on the basis of eq. 30 has recently been reported [12].

Finally, it should be mentioned that the non-zero mobility at high electrolyte concentrations has also been predicted in the theories [8–10] of the electrophoresis of a charged porous sphere as a model for polyelectrolytes, which is a system similar to that considered in the present paper. In particular, a mobility formula derived by Hermans and Fujita [9] on the basis of the linearized form of the Poisson-Boltzmann equation reads in our notation

$$\mu = \frac{zeN}{\eta\lambda^2}\left[1 + \frac{2}{3}\left(\frac{\lambda}{\kappa}\right)^2 \frac{1 + \lambda/2\kappa}{1 + \lambda/\kappa}\right], \tag{41}$$

which is almost identical with our approximate formula, eq. 39, yielding the same limiting form at high electrolyte concentrations (eq. 33). This implies that charged porous spheres and planar colloidal particles covered with surface charge layers exhibit the same behaviour at high electrolyte concentrations. Note, however, that in the limit of very high frictional coefficient of polymer segments ($\lambda \to \infty$), eqs 41 and 39 show different behavior. Namely, by identifying $(kT/ve) \cdot (zN/4vn)$ as ψ_0 (via. eq. 37), we see that in the limit $\lambda \to \infty$, eq. 41 reduces to Hückel's formula [13], which is applicable for small solid particles with thick electrical double layers or for particles having the same conductivity as the surrounding liquid, viz.,

$$\mu = \frac{2\epsilon_r\epsilon_0}{3\eta}\psi_0. \tag{42}$$

On the other hand, eq. 39 at the same limit becomes Smoluchowski's formula (eq. 31), which is applicable for large solid particles with thin electrical double layers. This discrepancy by a factor of 2/3 can be explained as follows. The theories of the electrophoresis of polyelectrolytes [8–10], dealing with a porous sphere, assume that the applied electric field is not perturbed by the sphere, as in Huckel's theory. On the other hand, in the present theory for a planar particle with a surface charge layer, the deformation of the applied field by the presence of the particle is implicitly taken into account by setting the applied electric field to be parallel to the particle surface, as in Smoluchowski's theory [11]. Therefore, by taking account fully of the deformation of the applied field by the presence of the particle, in other words, by taking proper account of the effects of the finite particle size, one would obtain the general mobility formula that yields both formulas (eqs 41 and 39) at different limits, as has been demonstrated for the case of the electrophoresis of solid colloidal particles [14,15]. Since, however, the dimension of biological cells is much larger than the double layer thickness $1/\kappa$ (≈ 10 Å under physiological conditions), the finite-size corrections to the present theory should be small.

References

1 E. Donath and V. Pastushenko, Bioelectrochem. Bioenerg. 6 (1979) 543.
2 R.W. Wunderlich, J. Colloid Interface Sci. 88 (1982) 385.
3 S. Levine, M. Levine, K.A. Sharp and D.E. Brooks, Biophys. J. 42 (1983) 127.
4 K.A. Sharp and D.E. Brooks, Biophys. J. 47 (1985) 563.
5 H. Ohshima and T. Kondo, Colloid, Polym. Sci. 264 (1986) 1080.
6 H. Ohshima and T. Kondo, J. Colloid Interface Sci. 116 (1987) 305.
7 H. Ohshima and T. Kondo, J. Colloid Interface Sci. 130 (1989) 281.
8 J.J. Hermans, J. Polym. Sci. 18 (1955) 527.
9 J.J. Hermans and H. Fujita, Koninkl. Ned. Akad. Wetenschap. Proc. B58 (1955) 182.
10 J.T.G. Overbeek and D. Stigter, Rec. Trav. Chim. 75 (1956) 543.
11 M. von Smoluchowski, Z. Phys. Chem. 92 (1918) 129.
12 S. Kawahata, H. Ohshima, N. Muramatsu and T. Kondo, J. Colloid Interface Sci. 138, 182 (1990).
13 E. Hückel, Phys. Z. 25 (1924) 204.
14 D.C. Henry, Proc. R. Soc. Ser A. Lon. 133 (1931) 106.
15 H. Ohshima, T.W. Healy and L.R. White, J. Chem. Soc. Faraday Trans. 2 79 (1983) 1613.